Abstracts of the physico-chemical literature in Japan

ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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1—GENERAL CHEMISTRY

On the isotopic weight of ^{12}C. K. Ogata. *Proc. Phys.-Math. Soc. Japan*, **III**, 22, 486—491 (1940).—The masses of all isotopes detd. by the doublet method depend on that of the substandards, ^{1}H, ^{2}D and ^{12}C. But one of these, ^{12}C, shows a discrepancy by different observers outside the probable error. This discrepancy is based on the disagreement in the measurements of the $^{12}C^{1}H^{4}$—^{16}O doublet. This mass difference can be checked by the combinations of the following doublets, $^{12}C^{1}H_{2}$—^{14}N, $^{14}N^{1}H_{2}$—^{16}O and $^{14}N^{2}$—$^{12}C^{16}O$, measured by Bainbridge-Jordan and Mattauch. The author takes the weighted means of these calcd. values and the direct measurement values for the mass difference $^{12}C^{1}H_{4}$—^{16}O. The results are as follows:

$^{12}C^{1}H$—^{16}O ($\Delta M.\ 10^{4}$)

Bainbridge Jordan	Mattauch
364.81 ± 0.41	363.662 ± 0.264
Aston	Present author
360.1 ± 1.6	364.2 ± 0.9

From these values, the isotopic weight of ^{12}C would be as follows:

Aston:	$12.00355 \pm 1.5 \cdot 10^{-4}$
Bainbridge-Jordan:	$12.00397 \pm 0.7 \cdot 10^{-4}$
Mattauch:	$12.003847 \pm 0.22 \cdot 10^{-4}$
Weighted mean.	$12.00387 1 \pm 0.33 \cdot 10^{-4}$.

In order to check the mass of ^{12}C, the author employed the following four methods, dispensing with use of $^{12}C^{1}H_{4}$—^{16}O; i.e. 1) From $^{12}C_{3}{}^{1}H_{4}$—^{40}A, $^{16}O^{2}D_{2}$—$^{40}A^{++}$ doublets, and masses of ^{1}H and ^{2}D; 2) From $^{12}C^{2}D_{4}$—^{20}Ne and $^{16}O^{2}D_{2}$—^{20}Ne doublets and mass of ^{2}D; 3) From $^{10}B^{1}H_{2}$—^{12}C, ^{10}B—$^{20}Ne^{++}$, $^{16}O^{2}D_{2}$—^{20}Ne doublets and mass of ^{2}D; 4) From $^{12}C_{2}$—$^{48}Ti^{++}$ and ^{16}O—$^{48}Ti^{+++}$ doublets. From these calcns., the author obtained the following values for the mass of ^{12}C, resp.:

1) 12.00036 ± 2.10^{-4} (Aston)
   $12.00387 \pm 0.3 \cdot 10^{-4}$ (Present author)
2) $12.00371 \pm 0.7 \cdot 10^{-4}$
3) $12.00366 \pm 2.0 \cdot 10^{-4}$
4) $12.0038 \pm 3.0 \cdot 10^{-4}$

Weighted Mean:

$12.00384 \pm 0.35 \cdot 10^{-4}$.

Subsequently, the author calcd. the masses of ^{1}H, ^{2}D and ^{12}C from all the principal doublets which have been measured by Aston, Bainbridge-Jordan, Mattauch and the present author. The values thus obtained are as follows:

$^{1}H = 1.008131 \pm 0.033 \cdot 10^{-4}$
$^{2}D = 2.014723 \pm 0.066 \cdot 10^{-4}$
$^{12}C = 12.003871 \pm 0.33 \cdot 10^{-4}$.

Author.

Molecular weight determination of vapours of low vapour pressure substances. I. Determination of vapour pressure and molecular weight of solid and fused selenium. K. Niwa and Z. Shibata. *J. Chem. Soc. Japan*, **61**, 667—676 (1940).—The authors have constructed an app., in which a torsion balance is added to the app. hitherto used for measuring the vapour press. of solid salts by means of the effusion method, and by which both the vapour press. of solid and the molecular weight of its vapour can be detd. Using this app., the vapour press. of TlCl was first

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redetd. to ascertain the accuracy of the app. and then the vapour press. of solid and fused selenium were detd. accurately and the number of atoms was calcd. in their vapour molecules which are considered to have different molecular states with variations in temp. Using the results obtained above, the following thermodynamic calcns. have been carried out: (i) heat of sublimation, heat of vaporization, melting point, and heat of fusion; (ii) free energy changes of sublimation and vaporization; (iii) degree of dissocn., partial press., dissocn. const., heat of dissocn. and free energy change of dissocn.

II. Determination of vapour pressure and molecular weight of solid tellurium. K. Niwa. *Ibid.*, **61**, 770—774 (1940).—Using the same app. as in the first paper, the vapour press. of solid tellurium and the number of atoms of its vapour molecule was detd. accurately and the following value obtained :—$Te_{2.00\pm0.5}$. Using the results obtained above, the following thermodynamic calcns. was carried out. (i) Heat of sublimation. $\Delta H_{638.1}=35.2_2\pm0.4_0$ kcal/mol. (ii) Free energy change of sublimation.

III. Determination of vapour pressure and molecular weight of solid antimony. K. Niwa and M. Yoshiyama. *Ibid.*, **61**, 1055—1059 (1940).—Using the same app. as in the first work, the vapour press. of solid antimony and the number of atoms in its vapour molecule was detd. accurately, within the temp. range, 500—560°C, and the following value was obtained :—$Sb_{4.00\pm0.15}$. Using the results obtained above, the following thermodynamic calcns. were carried out. (i) Heat of sublimation. $\Delta H_{803.1}=44.2_1\pm0.5_0$ kcal/mol. (ii) Free energy change of sublimation. Authors.

On the theory of solid helium. T. Nagamiya. *Proc. Phys.-Math. Soc. Japan*, **III**, **22**, 492—503 (1940). — The energy-volume curve of solid helium at absolute zero was calcd. under the assumptions that the mean positions of the atoms in it form a cubic close-packed lattice and that each atom is in the lowest quantum-mech. energy state in a mean field of force which is exerted to it by its neighbours. To calc. such a field the method employed by Lennard-Jones and Devonshire in their theory of condensation and critical phenomena was used, i.e. the 12 nearest neighbours were distributed on a sphere of radius equal to the shortest distance of the lattice. As the interatomic potential the Slater-Kirkwood and Margenau potentials were used. The agreement with expt. is good, especially when the Margenau potential is used, but owing to the roughness of both the exptl. data and theoretical calcn., it cannot be said with certainty that the fundamental assumptions are correct, especially considering the fact that other structures were not examd. and that the theory gives equally good result for liquid helium. Press. and compressibility and specific heat were also considered. Author.

The solid states of H_2 and D_2. M. Toda. *Proc. Phys.-Math. Soc. Japan*, **III**, 22, 503—507 (1940).—It is well known that crystal lattices of helium and hydrogen have singular properties due to their large zero point vibrations. In this paper the problem of solid hydrogen is investigated considering each molecule to be vibrating in its potential cage formed by the neighbours; and lattice spacing, heat of sublimation and compressibility are computed in terms of intermolecular forces of the Lennard-Jones type. Author.

On the constitution of ternary alloys. T. Hirone and T. Katayama. *Bull. Inst. Phys. Chem. Research*, **19**, 1419—1431 (1940).—The constitution of ternary alloys is studied by the calcn. of the free energy of the alloy. By the calcn. it is to be assumed that each atom has Z non-negligible potential energies when it is surrounded by Z nearest neighbours, and that the value of each potential energy will depend only on the kind of the atoms constituting the pair to which it belongs, and no variations in its magnitudes, due to change in compn., temp., etc. will be

admitted. It is assumed that each alloy which is considered in this work does not change its lattice as the compn. changes. As an example, the solubility limits in the equil. diagrams of Fe-Ni-Cu type and Ag-Cu-Ni type alloys are explained quite satisfactorily from the authors' theory. It is also theoretically concluded that the so-called "Mischungslücke" always exists, when each of three binary alloys constituting the sides of the ternary system makes a series of solid soln. in all proportion. Authors.

Crystal structure of silicon monoxide. H. Inuzuka. *Mazda Kenkyu Jiho*, **15**, 305—309 (1940).—The crystal structure of siliconmonoxide is detd. by X-ray. Its space groupe is $T_h^6 : a_0 = 6.4$ Å referred to the smallest cubic unit cell which contains 8-molecules of silicon monoxide. The structure leads to the conclusion that the silicon molecule is situated at the center of sheard tetrahedron consisting of four oxygen atoms.

Author.

Synthesis and X-ray analysis of gehlenite and anorthite. K. Akiyama. *J. Soc. Chem. Ind. Japan*, **43**, 757—758 (1940).—Gehlenite and anorthite synthesized from pure components were analysed by Debye-Scherrer's method. The epitome of synthesis is as follows. Lime, alumina and silica were mixed thoroughly in molar ratios, heated in a gas furnace for one hour at 1450°C and cooled then rapidly. The resulting products were finely ground and analysed. The results of X-ray analysis are given in the following table. The diffraction pattern of gehlenite showed that the sample does not contain $CaO \cdot SiO_2$ and $CaO \cdot Al_2O_3$. The same of anorthite indicated that the sample does not contain $CaO \cdot SiO_2$, cristobalite and mullite. Therefore, it was considered that every sample consists of a single compd. in which lime, alumina and silica are sufficiently combined with each other.

X-ray diffraction patterns of gehlenite and anorthite

No. of line	Gehlenite		Anorthite	
	d (Å)	*I*	*d* (Å)	*I*
1	3.757	m	4.900	f
2	3.412	ff	4.429	f
3	3.170	m	4.074	f
4	3.091	m	3.820	f
5	2.853	ss	3.685	s
6	2.701	ff	3.369	ff
7	2.537	f	3.124	f
8	2.422	s	2.819	ss
9	2.290	f	2.562	s
10	2.032	f	2.403	ff
11	1.918	m	2.317	ff
12	1.855	ff	2.247	f
13	1.803	f	2.128	m
14	1.747	ss	2.107	m
15	1.710	ff	2.022	f
16	1.610	ff	1.933	ff
17	1.507	m	1.878	ff
18	1.452	ff	2.827	s
19	1.367	m	1.751	s
20	1.315	ff	1.658	ff
21	1.276	ff	1.631	m
22			1.615	m
23			1.507	m
24			1.479	s
25			1.458	m
26			1.385	m
27			1.266	s
28			1.218	m
29			1.173	ff
30			1.159	ff
31			1.143	m
32			1.099	m
33			1.076	f

Author.

Analysis of calcined lime by X-rays. K. Akiyama. *Waseda Applied Chem. Soc. Bull.*, **17**, 26—27 (1940).—In order to exam. the difference between what is called light calcined lime and hard calcined lime, the X-ray diffraction diagrams of $CaCO_3$ calcined at 900—1,500° were compared. At 900° crystallization partly occurs, and its diffraction is the same as that above 900°. Accordingly, it is assumed that the difference of reactivity is due to the roughness of the

aggregation state. J. C. L.

On the study of crystobalite. H. Inuzuka. *J. Geological Soc. Japan*, **47**, 367—375 (1940).—This paper deals with the growth and transition temp. of crystobalite. The crystobalite is prepd. by five different ways as follows: (1) from fused silica; (2) from agate; (3) from metallic silicon powder; (4) from talc powder; (5) from silicon monoxide. The synthetic products were detd. by X-ray diffraction or electron diffraction methods. The lowest temp. at which the crystobalite is formed is about 600°C. Author.

On the determination of the inner potential by electron reflection method. T. Yamaguchi. *Proc. Phys.-Math. Soc. Japan*, **III**, **21**, 375—388 (1939).—A zinc-blende plane parallel plate bounded by cleaved surfaces was bisected to get two blocks of the crystal of equal thickness. Both blocks, one of which had etched surfaces and the other clean cleaved ones, were set in a close proximity to each other on a plane brass disc in such a manner that crystallographic axes of the two were nearly parallel, and were fixed on the crystal holder of the electron camera in such a position as to make the rotation axis, which is perpendicular to the electron beams, of the holder lie on them. Two sharp beams of electrons which were nearly parallel, one grazing to the etched and the other to the cleaved surface, were selected by a slit system and reflected to be photographed on the photographic plate. Thus, the mode of the increase of reflective index was investigated by a new method, by which the ratio of the wave-length and the spacing for each order reflection could be precisely known. J. C. L.

On light figures in single crystals of nickel and copper. M. Yamamoto. *Nippon Kinzoku Gakkai-Si*, **4**, 368—376 (1940).—The procedure of prepg. single crystals of nickel and copper by the method of slow solidification, and the app. for producing and obsg. light figures of crystals are described. Single crystals of nickel and copper were etched with aqu. solns. of acids and salts of various concns., at different time-intervals and light figures on the three principal crystal planes (100) and (111) were obsd. and examd. in detail in view of utilizing them for detg. the orientations of the said metal crystals. The symmetry characteristics of the light figures are naturally invariable, while their forms may, in general, vary with the etching reagent, the temp., and the time of etching. The most suitable light figures for the detn. of the crystal orientation are found to be those on (100) planes, except a few cases for nickel crystals. Author.

The specific gravity of the solution of metallic sodium in liquid ammonia. S. Kikuti. *J. Soc. Chem. Ind. Japan*, **43**, 568—570 (1940).—The author measured the specific gravity of liquid ammonia soln. of metallic sodium by the same app. and method as shown in the previous paper (*Ibid.*, **42**, 13 (1939)). The measurements were performed within the temp. range from −28° to 30°C and the concn. range from zero to satn. For the calcn. of specific gravity the correction was made as in the previous paper. The max. probable error of the measurement was below 0.1%, and the value of specific gravity is approximately accurate to the fourth decimal place. From the results of measurement the third and second orders to parabolic eqs. were applied for the relation between specific gravity and concn., and specific gravity and temp., resp., and then each const. was detd. from the above eqs. The values calcd. from the eq. of specific gravity versus temp. at various concns. and the values computed of the apparent molal volume and partial molal volume of sodium in liquefied ammonia soln. are tabulated resp. It is found that the molal volumes of liquefied ammonia soln. of metallic sodium are different in nature from water soln. and liquefied ammonia solns. of salts. Author.

Viscosity characteristics of lubricating oils as related to their chemical structure. B. Yamaguchi. *Rept. Aero. Research Inst. Tōkyō Imp. Univ.*, **15**, 111—136 (1940).—It is theoretically and exptly. evidenced that the viscosity-temp. coeff. at the same viscosity of liquids is an unique function of their chem. structure. For a number of synthetic high-molecular-weight hydrocarbons, the viscosity-temp. coeffs. at their resp. temps. having the same viscosity of 100 centistokes, e.i., the values of $-\left(\frac{d\nu}{dt}\right)_{\nu=100\ c.s.}$ have been calcd. by Walther's viscosity-temp. eq., and it is substantiated that the coeffs. calcd. are always definitely correlated with their chem. structure, with the conclusion that the greater the "entangling degree" of molecules of a hydrocarbon (which depends upon its molecular structure and is decidable under an assumption by the size or length of cyclic nuclei and paraffinic side chains together with the size and allocation of branched chains in the molecule), the smaller its value of $-\left(\frac{d\nu}{dt}\right)_{\nu=100\ c.s.}$ or its "structure viscosity index expressed by $-\left[\left(\frac{d\nu}{dt}\right)_{\nu=100\ c.s.}+5\right]\times 100$. Author.

Studies on the gypsum-urea, $4CO(NH_2)_2 \cdot CaSO_4$. I. Ternary system: $CO(NH_2)_2 - CaSO_4 - H_2O$. S. Uno. *J. Soc. Chem. Ind. Japan*, **43**, 273—274 (1940).—The hygroscopic nature of urea hinders its practical use as fertilizer in spite of the high nitrogen content (46.4%). The gypsum-urea or urea-calcium sulphate complex, $4CO(NH_2)_2 \cdot CaSO_4$, is more suitable as the fertilizer owing to its weaker hygroscopicity than urea itself. With a view of determining the fundamental conditions for the soln. method in the prepn. of gypsum-urea, the author has investigated the solubility isotherms for the ternary system consisting of urea, calcium sulphate and water at 0°—70°C. Author.

Studies on the hygroscopicity of chemical fertilizers. I. On the hygroscopicity of gypsum-urea, $4CO(NH_2)_2 \cdot CaSO_4$. S. Uno. *J. Soc. Chem. Ind. Japan*, **43**, 274—275 (1940).—Gypsum-urea or calcium sulphate complex, $4CO(NH_2)_2 \cdot CaSO_4$ discovered by Whittaker and coworkers attracted a great attention as a nitrogenous fertilizer owing to its weaker hygroscopicity than the urea itself. But gypsum-urea is decomposed by water to urea soln. and calcium sulphate dihydrate. $4CO(NH_2)_2 \cdot CaSO_4 + 2H_2O = 4CO(NH_2)_2 + CaSO \cdot 2H_2O$. The author measured by the isoteniscope method the vapor press. of the soln., saturated with both calcium sulphate dihydrate and gypsum-urea, in the temp. range of 15°—40°C. He then measured the moisture content of gypsum-urea at various humidities. Samples were placed in thin layers in small weighing dishes and laid aside at 30°C at relative humidities of from 50 to 85% in steps of 5%. Each sample was weighed daily. The dessication of the wet gypsum-urea was then examined. It was recognized that gypsum-urea becomes wet and develops a definite liquid phase accompanied by large gains in weight at above 80% relative humidity. The decompn. products of gypsum-urea by the absorbed water are combined again by slow drying, but not by rapid drying. Author.

Partition of sulphur dioxide between water and some immiscible solvent. H. Suzuki. *Bull. Inst. Phys. Chem. Research*, **19**, 1360—1363 (1940).—Partition of sulphur dioxide between water and an immiscribe solvent, such as chloroform, benzene, carbon tetrachloride was studied at 25°. Using a value $K_1=0.0127$, which was detd. by N. Yui as the first dissocn. const. of H_2SO_3 based on activity units, the concn. of undissocd. part of H_2SO_3 was calcd. by successive approximation from the following eq.:

$$C_{H_2SO_3}=\frac{(2AC+K_1)-\sqrt{(2AC+K_1)-4A^2C^2}}{2A},$$

in which C=analytical concn. of the acid, A=product of activity coeffs. of HSO_3' and H^+. With these concns. of the acid in aqu. solns. the partition coeffs. are found to be satisfactorily const., and the mean values are

are as follows: $C_{CHCl_3} : C_{H_2O} = 1.40$, $C_{C_6H_6} : C_{H_2O} = 2.03$. $C_{CCl_4} : C_{H_2O} = 0.516$. Author.

Supplementary note on the absorption of a gas and the form of the bubble. Y. Oyama and K. Iwase. *Sci. Papers Inst. Phys. Chem. Research*, **36**, 371—374 (1939).—Using an app. with a reformed nozzle, the absorption of the air contg. 36% CO_2 by N/100 and N/10 sodium hydroxide solns. was studied and it was found that the curve showing the relation between the absorbed amt. of CO_2 and the size of the bubble has a max. and min. points. J. C. L.

The reaction between magnesium oxide and stannic oxide in solid state. (Studies on the reactions in solid state at higher temperatures. V.) Y. Tanaka. *J. Chem. Soc. Japan*, **61**, 1023—1028 (1940).—Magnesium orthostannte ($2MgO \cdot SnO_2$) is the only stable molecular compd. which is formed by the reaction between magnesium oxide and stannic acid in solid state. At 1400°C the reaction proceeds almost completely in 10 hours. $2MgO \cdot SnO_2$ has a spinel structure and is soluble in $2MgO \cdot 4NHCl$. At the beginning of the reaction, however, the compn. of the reaction product is about $MgO : SnO_2 = 1 : 1$, in which the excess of stannic oxide contained in the orthostannate as solid soln., tends gradually to the normal molecular ratio of $2MgO \cdot SnO_2$. The heat of activation of the reaction in the temp. range between 1000 and 1100°C is about 100 Kcal, which is much greater than those of the reactions between titanic oxide and magnesium or calcium oxide. Author.

Studies on alunite. VIII. The mechanism of the thermal decomposition of alunite. I. Y. Asada. *Bull. Inst. Phys. Chem. Research*, **19**, 976—991 (1940).—External obsns. of the destruction of alunite during calcination as recorded in micro-photographs are reported and an account is given as to how fissures begin to appear at about 200°C. Then, by means of additional micro-photographs, magnified 500 times, the destruction of the crystal during calcination is explained. According to these data, when alunite is calcined for one hour at 600°C., the dehydration process is almost completed and the crystal is utterly destroyed, so that it begins to display amorphous properties. At 650°C., however, it begins to develop into a new crystalline phase and at 700°C. this tendency becomes extremely marked. At 800°C. the phenomenon draws to an end and destruction of the crystal commences owing to desulphuration. An exsothermal reaction of alunite during calcination was obsd. by means of differential thermoanalysis. It was found by this work that within a temp. range of 640—750°C., which is the interval between the dehydration and desulphuration points, there is a marked generation of heat.

IX. Relationship between the dehydration rate and melting point of potassium alum. *Ibid.*, 992—995 (1940).—In view of wide discrepancy of the informations by many workers regarding the melting point of potassium alum, which is variously put between 80 and 94°C., the author sealed the test material in a capillary tube and made careful obsns. of the moment-to-moment change classifyed in three stages, namely the wetting point, the quasi-melting and the complete melting point. It was found that the complete melting point of the substance is 90.6°C. and that the greater the dehydration rate of the test material is the higher the temp. rises, but at a dehydration rate of 75 per cent this phenomenon no longer occurs. Author.

The mutual transformation of raw cellulose and cellulose hydrate. V. Stability of the celluloses and their mutual transformation. K. Kubo. *J. Soc. Chem. Ind. Japan*, **43**, 198—202 (1940).—When the crystal lattice of cellulose hydrate formed by heating it in glycerine at 250°C is transformed into that of raw cellulose, cooling after heating does not exert much influence. In comparison of the X-ray photograph of the lattice at high temps. with that

after cooling down, it is found that the degree of transformation is slightly weakened after cooling. Therefore such a reverse transformation as from raw to hydrate is not considered to take place during cooling. From these results and a study of ζ potential, it is concluded that the effect of temp. on the stability of raw cellulose is small and that cellulose hydrate has a stability superior to raw cellulose at room temp., while its stability rapidly lowers with rising temp. There seems to lie a potential barrier between the two celluloses in question. J. C. L.

Studies on the organic molecular compounds. V. Formation of some crystalline organic molecular compounds. C. Shinomiya. *Bull. Chem. Soc. Japan*, **15**, 309—314 (1940).—The formation of "molecular lattice" construction in the crystalline state is not confined to ordinary organic compds.; it is probable that organic molecular compds. also form certain crystal lattices. According to the writer's studies (Parts I—IV), in the solid-liquid phase diagram of binary organic systems, the formation of crystalline molecular compds. is closely related to the configuration of the two components. The following two types of combination are distinguished here in the binary systems of naphthalene monosubstitution products:

(I) $HO \cdot H_7C_{10}.....(NO_2)_3 \cdot C_6H_3$

(II) $C_{10}H_7 \cdot NH_2$ .....$HO \cdot C_6H_5$.

Naphthols and naphthylamines, with very few exceptions, combine with nitro compds., and similar substances, quinones, and ketones in Type I, and with alcohols, amines, and acids in Type II, forming an ester or a salt type of combination. Halochromic phenomenon is marked in (I), but not in (II). Between the α- and β-monosubstituted naphthalenes, the tendency of the α-compd. to compd.-formation was usually greater in (I) and less in (II) than that of its isomer. This is elucidated by the "projection" of the substituent from the naphthalene nucleus which is more prominent in the β-position. When the compds. of a binary system have the same or similar substituents, the tendency to compd.-formation diminishes to a marked degree. The binary systems of trinitro compds. give no stable molecular compds. Author.

On explosive reactions of gases. I. Thermal explosion of oxyhydrogen gas at low pressures. S. Horiba and R. Gotô. *Proc. Imp. Acad.*, **16**, 215—222 (1940).—(I) Explosion induced by a heated platinum ribbon. Under a critical temp. of the platinum surface the intensity of the surface reaction is an important factor in the occurrence of explosion. When the surface reaction is sufficiently intense, inflammation takes place near the surface and the flame propagates outwards. The influence of the pretreatment of the platinum ribbon suggests that there exists some poisoning effect of the reaction product, presumably the water vapour adsorbed on the surface. (II) Explosion in an externally heated vessel. It was found that many expt. conditions as well as the nature of the surface have much influence upon the limiting curve of explosion. (III) An expt. which shows the heterogeneity of the thermal explosion. It was shown that in the explosion at the upper limit, a reaction zone or flame starts from the wall of the vessel and propagates inwards. From these expts. it is concluded that the low press. explosion is not a homogeneous process in the gaseous phase. Authors.

On explosive reaction of gases. I. Explosion limits of oxyhydrogen gas. S. Kimata, N. Aomi and R. Goto. This Journal, **15**, 42—53 (1941).

Studies on silvering of glass, effect of organic acids on the formation of a silver mirror. T. Inagaki. *Bull. Electrotech. Lab.*, **4**, 712—714 (1940).—The chem. formation of a silver mirror on glass is influenced by the presence of foreign substances in silvering soln. A large variety of organic acids were added into formalin reducing soln.,

so that the quantity of every organic acid was such as 0.001 mol per 1l. of the final soln. The results are summarized as follows; (1). Lactic acid, formic acid and acetic acid greatly increase the deposition of silver: and tataric acid, benzoic acid and succinic acid increase it in some degree, while citric acid and picric acid exhibit a neg. effect. (2). A smooth, fine surface of a silver mirror without traces of pin-holes results upon the addition of these acids, even if citric acid is introduced. With picric acid this is not the case. The formation of a smooth, uniform mirror by the addition of these acids is considered to be the result of their acting as a protective colloid upon reduced silver particles.

Author.

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

The slowing down of neutrons from (Ra+Be) in a large volume of water. T. Hagiwara and E. Suito. *Proc. Imp. Acad.*, **16**, 543—548 (1940).—In order to ascertain whether and to what extent the chem. decompn. of hydrogen peroxide soln. takes place under neutron irradiation, the 0.02 molar soln. was put in a number of thin walled paraffin lined copper tubes which were immersed at varying distances from the source of 50 mg Ra and Be in a large volume of water. The effect on the chem. decompn. due to the neutron source, shielded by lead, was compared with that of a pure Ra source of the same strength under the same conditions, the natural decompn. being taken into account. From the curves of the decompn. with respect to the distances of the specimens from the source, it was shown that the neutron-curve possesses a remarkable max. at about 11 cm of water from the source and a small second one at about 20 cm of water. This appearance of max. was regarded as an evidence of high efficiency for the decompn. only by the neutrons. A series of further expts. of neutron irradiation was also attempted to obs. how the magnitude of the decompn. effect varied with the introduction of boric acid or $CdSO_4$ into the soln. The presence of boron in the soln. caused a striking increase of the decompn. The general form of the curve without the addition was very similar to that with boron, the corresponding parts of the max. being found essentially consistent with each other with respect to the distance from the source. The comparison between the curves of B and Cd showed the earlier occurrence of the max. with B than with Cd. Accordingly it was concluded that the remarkable decompn. of hydrogen peroxide at the region of the first 11 cm of water is most sensitive to those energies of slow neutrons which are most effectively absorbed in boron. Thus it was supposed that the most effective slow neutrons in question are those which diffuse in a considerably large number of collisions with protons of water. The second occurrence of the max. at the distant part of water is suggested as an approximate indication of the number of hard components of the neutrons emerging from the source (Ra+Be) surrounded by lead. Authors.

Resonance capture of slow neutrons and γ-rays. I. Nonaka. *Mazda Kenkyu Jiho*, **15**, 1—8 (1940).—In the capture of slow neutrons, by such atom nuclei as become radioactive the existence and energy of group neutrons of resonance capture were detd. by the γ-ray radiated in the capture of slow neutrons. By inserting a paraffin plate between D+D neutron source and the sample (Fe, Cd, Hg, and Bi), the relation between the intensity of γ-ray and the thickness of the paraffin plate was examd. J. C. L.

Relative number of gamma-ray quanta emitted per capture of a thermal neutron. I. Nonaka. *Mazda Kenkyu Jiho*, **15**, 310—314 (1940).—The relative number of gamma-ray quanta emitted per capture of a thermal neutron was exptl. found to be 0.64, 0.74, 1.00, and 0.82 for Cl, Ag, Cd, and Hg resp. These results were compared with those of other investigators. The same number was also calcd. from the binding energy of a neutron to the nucleus, and was found to agree approximately with the exptl. obtained results. Author.

On the angular distribution of fast neutrons scattered by the atoms. III. T. Wakatuki. *Proc. Phys.-Math. Soc. Japan*, **III**, **22**, 430—441 (1940).—The angular distribution of fast neutrons scattered by proton, carbon, aluminium, iron, tin and lead was measured for both D-D and Li-D neutrons. The differential scattering cross section for 3 Mev neutrons was found to have a max. at about 20 degrees for most elements except proton. In the scattering of Li-D neutrons this max. does not appear. The data on the scattering of neutrons by protons which were obtained in the previous work are discussed with the addition of the new data. The scattering cross section for C-D neutrons measured by Amaldi and others are utilized in these discussions. A very marked anisotropy is necessary to account for the present exptl. results. Author.

A note on the Stark-effect of anomalous lines of mercury spectrum. Y. Ishida and S. Hiyama. *Sci. Papers Inst. Phys. Chem. Research*, **37**, 227—231 (1940).—The authors studied the Stark-effect of the lines which belong to neither normal nor ionized mercury spectrum in the same condition as Hg I spectrum which had already been reported. They confirmed exptl. the existence of the terms 5504 and 7238 which had been proposed by K. Murakawa (*Sci. Papers Inst. Phys. Chem. Research*, **20**, 285 (1933) and *Proc. Phys.-Math. Soc. Japan*, **18**, 345 (1936)) as having the electron configuration $5\,d^9\,6\,s^2\,6\,p\ {}^1D_2$ and $5\,d^9d\,s^2\,6\,p^2\ F^4$ resp. The numerical data on these lines are given. Authors.

On the appearance of neon spark-lines under the influence of an external magnetic field. Y. Morimoto. *J. Sci. Hiroshima Univ.*, **A**, **10**, 253—259 (1940).—The quartz capillary portion of a Geissler-tube containing pure neon gas was transversely set between the poles of an electromagnet. The intensity of the NeI spectral lines was enhanced as soon as the weak current was supplied to the magnet. The NeII spectral lines did not appear as long as the magnetic field was weak. While the magnetic field was being increased from about 3×10^3 to about 7×10^3 Gauss, the lines belonging to the NeII spectrum appeared in abundance, and showed a marked increase in intensity; this seems to be a max. value. On the other hand, it was found that the needle spark gap length connected between the electrodes of the neon discharge-tube was extraordinarily increased when the magnetic field was transversely applied to the discharge-tube. If the increase of length of the needle spark gap were brought out only by the increase of resistance of the discharge-tube, the length of the needle spark gap should be max. when the resistance of the discharge-tube was infinite. To the author's surprise, however, the needle spark gap length was 18.6 mm when the discharge-tube was taken away; but the lengths of spark gap with strong magnetic field were always greater than this value. For example, the needle spark gap length was about 31 mm when the magnetic field was 12×10^3 Gauss. This phenomenon was verified by using a sphere spark gap. The explanation needs further investigation.
Author.

The effect of solvents on the internal rotation of carbonic ester. M. Yasumi. *J. Chem. Soc. Japan*, **60**, 1208—1224 (1939).—The dipole moment (m) of

$CO(OCH_3)_2$ and $CO(OC_2H_5)_2$ was calcd. between $-40°$ and $+70°$, using benzene, hexane and heptan as solvents. In every case, m tends to be raised with rising temps. Taking into consideration the data of the dipole moment of these two substances in gases obtained by other investigators—Kubo, Morino, and Mizusima, it was inferred that there exists vibrational rotation of the partial dipole about the two C—O single bonds of $=C<^{O-R}_{O-R}$ having the position which is explained by the data of the dipole moment as its centre. Moreover the estimation of the electrostatic force and repulsive exchange force of the dipole in the molecule leads to the suggestion of the probable existence of 2 kinds of stereoisomer. J. C. L.

Studies on internal rotation of ethane, propane and butane derivatives by the Raman effect. N. Nakamura. *J. Chem. Soc. Japan*, **60**, 1010—1019 (1939).—In comparison of the Raman spectra of the compds. which are generally considered to possess the axis of internal rotation, such as those of liquid and solid 1-chlor-propane, 1-brom-propane, 1-iodo-propane, 1-brom-butane, 1-ethylene-glycol, 1-ethylene-chlorhydrine and ethylene-iodo-hydrine, and that of ethylene-brom-hydrine, number of the Raman lines of the said solid compds. is approximately 1/2 of those of the liquid compds. This phenomenon can be well explained by the supposition that the characteristic molecular vibration presented in the Raman spectra shows the mixing of 2 kinds of types in liquid and only 1 kind of type in solid. But, the Raman spectrum of ethylene-iodo-hydrine is much the same in solid and liquid, and it seems that also in solid 2 kinds of forms are mixed. The author proposes the molecular model of solid $CH_3 - CH_2 - CH_2 - X$. J. C. L.

Raman effect in ethane and butane. S. Nakamura and E. Kanda. *J. Chem. Soc. Japan*, **60**, 1275—1278 (1939).—The Raman effects of solid and liquid butane were examd. at low temps. As to what is considered to represent chain vibration, there are 12 lines in liquid and 3 lines in solid. From this fact, it is considered that there exists a trans form in the solid state and there also co-exists a form obtained by rotation of 120° from the trans form. In the liquid state at relatively high temp., frequent internal rotations occur round the minute points of potential energy, having the C—C bond as the axis. By means of some app. the Raman line of liquid ethane was effectively obsd. at -140—$150°$ and its wave number is tabulated with the values which have hitherto been obsd. J. C. L.

Raman effect and dipole moment in relation to free rotation. XII. Raman spectra of ethylene chlorhydrine, *n*-propyl chloride, and *n*-butane in the liquid and solid states. S. Mizushima, Y. Morino and S. Nakumura. *Sci. Papers Inst. Phys. Chem. Research*, **37**, 205—215 (1940).—The Raman spectra of ethylene chlorhydrine, *n*-propyl chloride, and *n*-butane were obsd. in the liquid state as well as in the solid state, and the conspicuous difference between the spectra of these two states (i.e. the disappearance of many Raman lines on solidification) was found for each of these three substances. An explanation for this expt. result is suggested as follows. In the liquid there exists a dynamic equil. between the two molecular forms, while in the solid state only one of them is stable. This stable form in the solid state is the trans form for ethylene chlorhydrine and *n*-butane, while it is a Gauche form in the case of *n*-propyl chloride. The chain frequencies of the trans form of ethylene chlorhydrine are calcd. and the assignment of low frequency lines is made.

Authors.

Studies on the cathodo-luminescence of inorganic solids containing manganese. E. Iwase. *Sci. Papers Inst. Phys. Chem. Research*, **38**, 67—80 (1940).—Under the excitation by cathode-ray bombardment, the luminescence given by numbers of oxides, sulphates, phosphates, borates and silicates, to

which manganese was added in a small quantity, was investigated. The luminescence spectra of some luminescent solids were spectrographically studied. Several cases are pointed out, in which the conception proposed by Tiede concerning the luminescence colour and the difference between the atom radius of the metal component of ground material and that of activating metal seems to be applicable. Author.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

On the energy states of valency electrons in some metals. I, 4. Revisions to the "Nature of electrode potential of zinc and hydrogen and the mechanism of catalytic action of metal surface". M. Satô. *Sci. Repts. Tôhoku Imp. Univ.*, **I, 29**, 87—112 (1940). —The absolute values of the potential barrier in the following electrodes were recomputed and corrected as follows: for normal hydrogen electrode at 25°C, 4076 mV, and for the surfaces of

Zn-crystal	(0001)	(10$\bar{1}$0)	(11$\bar{2}$0)	(10$\bar{1}$1)	(11$\bar{2}$1)
in H_2SO_4-soln.	3202	3226	3240	3252	3264
in $ZnSO_4$-soln.	3318	3319	3321	3311	3315

at 25°C in mV. The above value for hydrogen corresponding to ν 32938 cm^{-1}, was compared with molecular levels of H_2 and it was found to be in magnitude between B, $1s\sigma$, $2p\sigma$ $^1\Sigma u$, V=0: 33561 and V=1: 32262 cm^{-1} where V is the vibrational quantum number. The explanation of the exptl. result of the photo-electric phenomena of adsorbed hydrogen obtained by R. J. Cashman and W. S. Huxford, (*Phys. Rev.*, **48**, 734 (1935)) is revised, and a special consideration on the mech. of detaching photo-electron from H_2-molecule in the secondary max. in the photo-electron emission, is also made. By analogy of this explanation, the mech. of the photo-electron emission by zinc in the excitation of photon with energy near its threshold value is given. Author.

Solution pressure of pure Al. II. I. Igarasi and S. Kodama. *Nippon Kinzoku Gakkai-Si*, **3**, 428—430 (1939).—As the exptl. results obtained by Poggendorf's compensation method concerning the soln. press. of Al were not so satisfactory, extremely slight variations caused by impurities, introduced gas and the surface of the electrode were examd. by means of a valve voltmeter with a UX-54 valve of little Grid current. (1) The change of the soln. press. is not essentially different from that in the preceding report, the obsd. value of 99.99% Al agrees with $E_h \fallingdotseq -1.22$ V. The values of both 99.8% Al and 99.5% Al reach a max. and then fall and agree with $E_h \fallingdotseq -0.82$ V. The value of Al-Fe (1%) does not agree with that of Al-Fe (5%). (2) The change of the soln. press. till it becomes const. and the phenomena at the time H_2 or O_2 is introduced seem to have close relation to the local current. (3) The change of the soln. press. caused by the introduced gas is not probably due to the formation of a gas-metal electrode. (4) The surface condition of the electrode exerts a marked influence on the soln. press.: when there is no influence of film, a smooth surface is lower than a scratched one with respect to the soln. press. J. C. L.

Osmosis. II. Osmosis of salt solution. R. Goto. *Kyoto Furitu Ika Daigaku Zassi*, **27**, 213—230 (1939). — Yasumaru's osmometer was equipped with 2 incompletely dried collodium capsules of standard potential difference of 5 and 15 mV, each of which contained N/50, N/200 and N/800 solns. of KCl, NaCl, LiCl, $MgCl_2$ and $CaCl_2$. It was immersed in 150 c.c. of distilled water and the rise and fall of water column was obsd.

for 6—73 hours in a thermostat kept at 18°. In each case, the water column reaches a max. in a definite lapse of time and then falls. In the case of monovalent two component electrolyte, the larger the standard potential difference is, the longer the time taken for the electrolyte to reach a max. is, and the higher the concn. of the soln. is, the shorter the time becomes. The height of the max. point, however, is much the same, being independent of the standard potential difference. In the case of the same standard potential difference and concn., the order of the height of the max. point is K>Na>Li. As to a bivalent three component electrolyte, the standard potential difference of collodium capsule is mostly large, and when the soln. contained in the capsule is remarkably dilute, it takes many hours (50—70 hrs.) for the soln. to reach a max. J. C. L.

The Faraday effect and the conductivity of electrolytic solution. A. Okazaki. *Mem. Ryojun Coll. Eng.*, **12**, 33—43 (1939).—It has been found that the equivalent percentage increments Δ of Verdet's const. ω and the rotation const. $D=\frac{n\omega\lambda^2}{(n^2+2)^2}$ of the solns. of alkali halides have linear relations with the degree of dissocn. i or the equivalent conductivity Λ over the concen. range of m<6 : $\Delta=B+(A-B)\,i=B+(A-B)\frac{\Lambda}{\Lambda_0}$. By graphical extrapolation to $i=1$ or 0, the values of A and B concerning ω and D have been detd. The A-value of an electrolyte may be composed additively of the moduli characteristic of the component ions. The molecular rotations of the salts in dissocd. and undissocd. states have been evaluated by using the values of A and B.

Author.

On the mechanism of hydrogen electrode process: Reply to the criticism of Frumkin and his collaborators. J. Horiuti. *Sci. Papers Inst. Phys. Chem. Research*, **37**, 274—301 (1940).—The present position of the dual theory of the catalytic and the electrochem. mech. of the hydrogen electrode process [Horiuti and Okamoto, *Sc. Pap. I. P. C. R., Tokyo*, **28**, 231 (1936)] and Frumkin's criticism of it are summarized in three points. In reply to the first objection raised against the electrochem. mech. based on the assumption of ideal gas-like behaviour of hydrogen atoms on the electrode surface, it is shown that the peculiar situation of hydrogen atoms, giving rise to a weak but far-reaching repulsive potential among hydrogen atoms or groups of particles involving hydrogen atoms mutually or among those and other particles, preclude the validity of the ideal gas-like treatment, when the electrode surface is even only moderately populated and that the incorporation of the situation with the theory of the electrochem. mech. leads to conclusions in satisfactory agreement with expts. In reply to the second objection raised against the catalytic mech. or the recombination theory on the ground of Frumkin's exptl. results on the effect of electrolytes upon the current density, it is shown that the effect claimed by Frumkin is only apparent owing to an incomplete control of exptl. conditions and that Frumkin's result, when properly interpreted, leads, in conjunction with other exptl. results, to a conclusion in accordance with the catalytic mech. As to the third objection raised against the catalytic mech. on the ground of the numerical discrepancy between the rate of the electrode process predicted by the theory and that obsd., it is pointed out that the extent of the discrepancy is rather inside that expected from the inaccuracy of the fundamental data used for the theoretical calcn. and from the uncontrolled fluctuation of the exptl. data. It seems impossible to draw any conclusion against the dual theory from available exptl. data including those contributed by Frumkin and his collaborators. Author.

Studies on the anodic behaviour of tin. IV. H. Itô. *Nippon Kinzoku Gakkai-Si*, **4**, 393—396 (1940).—The author has hitherto studied the passivity of pure and

impure tin anodes, which contain Cu, Pb, or Bi as impurity. The present paper concerns also that of Sb- or As-containing anode. The effect of Sb, when containing in the amt. of 0.5%, is not so noticeable, but in the case of 5% the anode passifies considerably fast. The additional increase up to 10% shows only a small effect. When the potential on the passive anode is raised to some value, there comes out a phenomenon which may be considered as an another passivity. This cause may be as follows: owing to the high anode potential Sb is forced to dissolve, which hydrizes, and fills the pore in the primary passive film with basic antimony sulphate making current difficult to pass, and it seems also to promote the passivity. Author.

On the anodic behaviour of Cu_6Sn_5. H. Itô. *Tech. Repts. Kyushu Imp. Univ.*, **15**, 114—118 (1940).—The anodic behaviour of Cu_6Sn_5 in H_2SO_4 and in HCl was studied. The cross-section of a bar of 5 mm dia. of this alloy serves as a sample anode, the compn. of which is 36.8% Cu and 63.2% Sn, slightly higher for Sn than the theoretical value (39.1% Cu, 60.9% Sn). In H_2SO_4 the anode remains active for a short time after the circuit has been closed, then suddenly becomes passive, the current breaks and the anode potential springs up rapidly. On raising the bath voltage oxygen begins to discharge on the passified anode at the anode potential of about +2.3—2.4 V. The sign of dissolution of Cu was not obsd. at all. The anodic behaviour of this compd. in HCl is quite characteristic. The alternating passivation and activation of anode, namely, the periodic dissoln., is obsd. The decompn. of Cu_6Sn_5, followed by the dissoln. of Cu is forced by the high anode potential in the passive period, thed the anode becomes active, resulting in the accumulation of insoluble Cu_2Cl_2 on its surface, which makes anode passive, and this circle is repeated on and on. Author.

Studies on the catalytic oxido-reduction of some metallic complex salts. XII. Reduction of quinone by hydrogen in the presence of [Pd*en*]Cl_2. Y. Shibata and E. Matsumoto. *J. Chem. Soc. Japan*, **60**, 1173—1176 (1939).—The catalytic reduction of quinone by hydrogen was obsd. in the dark, using a complex salt [Pd*en*]Cl_2 and it was ascertained that the addition of the complex salt leads to the increase in the hydrogen adsorbed amt. of quinone. The reduction was also obsd. at varying ratios of quinone to the catalyst used. J. C. L.

The change of the concentration in the solution by electrolysis. S. Kaneko. *Bull. Electrotech. Lab.*, **4**, 676—678 (1940). —By the extension of Sand's theory (*Phil. Mag.*, **1**, 45 (1901)) the change of the concn. by electrolysis near the plane or cylindrical electrode is considered. Author.

Deposition of metallic powder by electrolysis. S. Kaneko and K. Kawamura. *Bull. Electrotech. Lab.*, **4**, 821—823 (1940).—The following relation is verified by the expt. with solns. of copper and zinc sulphate $i\,\tau^{1/2}=$const., where i is the current density, τ the time needed before the metallic powder begins to appear on the cathode. Authors.

On the dissociation constants of sulphurous acid. N. Yui. *Bull. Inst. Phys. Chem. Research*, **19**, 1229—1236 (1940). —The true dissocn. consts. of sulphurous acid were detd. by means of a glass electrode at 25°C, measuring the pH values of the acid of various concns. and also the pH value at each stage of titration of the acid with sodium hydroxide soln. The cell used was as follows:

Hg	HgCl, KCl (s) (sat.)	H_2SO_3 (aq)	glass
0.1 *N* CH_3COOH / 0.1 *N* CH_3COONa	KCl, HgCl (sat.) (s)		Hg

From the pH values of the acid the first dissocn. const. was computed to be 0.0136, and from the result of titrations 0.0125 and 0.0121 resp. Hence a mean value 0.0127 was finally adopted. On the basis of the result of titrations the second dissocn. const.

was found to be 6.16×10^{-8} and 6.31×10^{-8}, and a mean value 6.24×10^{-8} obtained. Consequently

$H_2SO_3(a=1) = H^+(a=1) + HSO_3^-(a=1)$, $\Delta F^\circ_{298} = 2{,}587$ cal ;

$HSO_3^-(a=1) = H^+(a=1) + SO_3^{--}(a=1)$, $\Delta F^\circ_{298} = 9{,}828$ cal.

Author.

On the dissociation constant of hypochlorous acid. H. Hagisawa. *Bull. Inst. Phys. Chem. Research*, **19**, 1220—1228 (1940).—The pH-values of hypochlorous acid of various concns. (0.095—0.0038 mol/*l*) and and of the mixts. of acid and sodium hypochlorite were measured at 25°C by means of a glass electrode.

Hg | HgCl, (s) KCl (sat.) | 0.1 *N* acetic acid, 0.1 *N* Na-acetate | glass | HClO (aq) or HClO + NaClO | KCl (sat.), HgCl (s) | Hg

The dissocn. const. of the acid was found to be $K_a = 3.01 \times 10^{-8}$ in the former measurements, and $K_a = 2.95 \times 10^{-8}$ in the latter. The mean value $K_a = 2.98 \times 10^{-8}$ was adopted. Hence $HClO(a=1) = H^+(a=1) + ClO^-(a=1)$, $\Delta F^\circ_{298} = 10{,}266$ cal ;

$\frac{1}{2}Cl_2 + \frac{1}{2}O_2 = ClO^-(a=1)$, $\Delta F^\circ_{298} = -8{,}844$ cal.

Author.

On the frictional electricity of the fibres. I. Effect of humidity and discharge. C. Matano. *J. Soc. Chem. Ind. Japan*, **43**, 666—678 (1940).—The quantity of the frictional electricity which was generated at the spinning machine on the cellulosic fibres was measured under various conditions and the following conclusions were drawn empirically. (1) There exists a relation $\rho_0 = Ae^{-\alpha h}$ between the line density ρ_0 of the generated frictional electricity on the fibre and the relative humidity h : A, e and α are consts. independent of h. (2) A relation $I = HV^{\frac{3}{2}}$ holds good among the time rate of discharged electricity I of the fibre and its elec. potential V : H is a const. independent of V but increasing rapidly with h. Author.

The heat of formation of manganese nitride. S. Sato. *Bull. Inst. Phys. Chem. Research*, **19**, 28—36 (1940).—From the formula of the specific heat of Mn_6N_2 proposed by the author and the dissocn. press. of Mn_6N_2 at 910° and 1,175° calcd. by Schukow, the heat of formation of Mn_6N_2 was found to be $8Mn(\alpha) + N_2 = Mn_6N_2 + 79.7_5$ Cal. as the mean. From the author's formula of the specific heat of Mn_6N_2 and Mn_5N_2, Schenck and Kortengrüber's dissocn. press. ($8/3\ Mn_5N_2 \rightleftarrows 5/3\ Mn_6N_2 + N_2$), and the above-mentioned heat of formation, $5Mn(\alpha) + N_2 = Mn_5N_2 + 57$ Cal. was thermodynamically obtained as the heat of formation of Mn_5N_2. This value agrees well with other thermochem. values (57.8 Cal. and 56.8 Cal.), and so the said heat of formation of Mn_6N_2 is considered to be correct. J. C. L.

Approximate calculation of free energy and equilibrium constant from thermochemical value and its application. W. Sakai. *Tech. Repts. Kyushu Imp. Univ.*, **14**, 263—298 (1939).—With respect to thermodynamical formulae showing the free energy or equil. const. as a function of temp., various approximate formulae assumed are compared and criticized in order to make approximate calcn. correctly and simply. J. C. L.

Hydrocarbons from carbide, thermodynamics. R. Negishi, O. Kimura and O. Kamiike. This Journal, **15**, 31—41 (1941).

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

Studies on the oiliness of the liquids. IX. Measurements of the static friction coefficients of cyclic compounds for glass surfaces. T. Ise-

mura. *Bull. Chem. Soc. Japan*, **15**, 288—291 (1940).—(1) The measurements of the static friction coeffs. of cyclic compds. for glass surface are reported. (2) It is noticed that no cyclic compd. is a good lubricant, although *m*-cresol and cyclohexanol among them are moderately active as lubricant. Author.

Study on rhythmic precipitates. I Electrical study. A. Yanagihara. *Bull. Inst. Phys. Chem. Research*, **19**, 1251—1260 (1940).—The variation of electomotive force of an ion concn. cell consisting of two platinum electrodes inserted into a gelatine gel, in which rhythmic reaction of silver chromate occurs, was obsd. by means of a quadrant electrometer. The results are shown by numerous graphs and photographs. The graphs show e.m.f. variation due to the rhythmic pptes. under various conditions, namely, concn. change of inner electrolyte and interchange of inner and outer elyt. The case of outer elyt., to be diffused into a gelatine gel containing no inner elyt., was also investigated. In this case a remarkable difference of electricity is recognized in the diffusing front (forming a double layer of Ag^+ and NO_3^- ions) of silver nitrate and that of potassium dichromate. Author.

Studies on the effects of ultrasonic waves on colloid-phenomena. VII. Experiment on the effects on cane sugar solution. N. Sata and Y. Harisaki. *Bull. Chem. Soc. Japan*, **15**, 180—185 (1940).—In order to study the effects of ultrasonic waves on chem. bonds, the inversion of the cane sugar was investigated. 10% soln. of specially purified cane sugar was irradiated with ultrasonic waves of 450 KC for 30—60 minutes in fused quartz-vessel. The inversion was estimated by both chem. (by reducing power detn.) and phys. (by polarimetry) methods. Although an occurrence of trace of inversion was detected, it could not be concluded as pure ultrasonic effect, because the exptl. value was smaller than the limit of accuracy of analytical methods. Authors.

On the dialysis of platinum-carbonyl sol. I. Sano. *Bull. Chem. Soc. Japan*, **15**, 207—208 (1940).—The platinum-carbonyl sols of red colour prepd. from 0.02 and 0.05% aqu. solns. of chloroplatinic acid were dialyzed in the atmosphere of carbon monoxide, as they would be converted into platinum sols when treated in the air, until freed from chlorine ions. The sols obtained by the process are just the same in appearance as they were. This implies that the particles in the red sols, whether dialyzed or not, are fundamentally constituted from platinum and carbon monoxide or platinum-carbonyl.

Author.

Silver organosol by the reaction between chlorinated oil and silver oxide. T. Matsumoto and S. Iwai. *J. Soc. Chem. Ind. Japan*, **43**, 27—29 (1940).—The oil which has not been chlorinated generates metallic soap by reacting with silver oxide, while chlorinated oil generates silver colloid, irrespective of the amt. of chloride contd. Silver organosol consists of a large amt. of metallic silver and a small amt. of silver chloride. When a certain solvent is added to silver organosol, a part of the oil dissolves in it, and a part rich of colloids is left as the lower layer. When this procedure is repeated for the part rich of colloids, concd. silver organosol is obtained. From a mixed solvent of butyl-alcohol and ethyl-alcohol, a sol containing 95.4% was obtained whose property is described. It is concluded that the formation of sol is due to the fact that silver oxide oxidizes chlorinated oil and the reduced nickel diffuses in oils and fats.

J. C. I.

Action of gelatin-gels in sodium chloride solution. T. Hasegawa. *Bull. Japanese Soc. Sci. Fisheries*, **9**, 61—63 (1940).—The cubes of gelatin or agar-agar gel of the same size were immersed each in an excess of sodium chloride solns. of about 0, 10, 15, 20 per cent and kept either at room or low temp. Each time before and after immersing, the weight and water content of

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each cube were obsd., and the salt content was measured at intervals. The author thinks that the phenomena that occurred in this immersing, which is similar to fish curing, were very complicated, and, therefore, only the data are here indicated. Author.

Velocity of adsorption by magnesia of light and heavy water vapours. F. Ishikawa and I. Kanamori. *Bull. Inst. Phys. Chem. Research*, **19**, 1213—1219 (1940).—The velocity of adsorption of light and heavy water vapours by magnesia which was prepd. by dehydrating the hydroxide at low temps. has been measured at 30°, 22°, and 15.5° by the use of a quartz spring balance. The velocity may be expressed by the eq. proposed by Bangham and Sever, that is, $\ln(S/(S-x)) = kt^n$, where S is the satn. value of adsorption, x is the value at the time t, k and n are the consts. By comparing the adsorption velocities of these vapours, it is concluded that a diffusion of these vapours through the capillary pores of magnesia forms an important part of the velocity of adsorption. Authors.

Catalytic activity of phthalocyanines in the autoxidation of linseed oil and methyl linoleate. B. Tamamushi and S. Tohmatsu. *Bull. Chem. Soc. Japan*, **15**, 223—226 (1940).—The catalytic action of metallic phthalocyanines towards the autoxidation of linseed oil and methyl linoleate is demonstrated. Chloriron phthalocyanine is remarkably effective as catalyst, whereas copper- and magnesium phthalocyanine are slightly effective. Authors.

The action of magnetised ferromagnetic catalyst. E. Ogawa. *Tech. Repts. Kyushu Imp. Univ.*, **14**, 243—261 (1939).—The theory of para-ortho hydrogen conversion, i.e. the action of a paramagnetic substance on nuclear spins or on' spins of valence electrons forming a pair is described and the action of reacting molecules on spins of valence electrons in the presence of magnetised ferromagnetic catalyst discussed and it is concluded that the magnetisation of ferromagnetic substance retards the reaction. The reaction between C_2H_4 and H_2 and that between allyl bromide and HBr in the presence of Ni-wire and new K.S. steel used as catalysts justifies the conclusion qualitatively. As to the polymerisation of C_2H_2 and H_2 or meta-acrylic acid methyl ester, the combination of the catalyst with reacting substances makes the catalytic condition so complex that the effect of magnetization is uncertain. When an ether soln. of $Fe(CNS)_3$ and hydrochloric acid are placed to-gether in the magnetic field, the formation of $FeCl_3$ is promoted. From this phenomenon it is inferred that on the boundary surface the perturbation is caused by the magnetic field. Hence, it is concluded that this perturbation may affect the rate of the reaction between C_2H_4 and H_2. When C_2H_4 and H_2 are made to react on the constantan wire charged with high-tension current, the reaction velocity tends to become low with increasing tension. This is probably due to the perturbation of constantan for the adsorbed molecules of C_2H_4 and H_2. J. C. L.

Thermal decomposition of nitrogen-pentoxide by platinum surface. I, II. N. Sasaki and Y. Hiraki. *J. Chem. Soc. Japan*, **61**, 812—817, 818—826 (1940).—To study the energy exchange between gas molecules and solid surface, the authors measured the probability of activation of nitrogen-pentoxide molecules at 0°C by hot platinum surface at very low press. (10^{-4}—10^{-5} mmHg). Decomposition begins to take place at about 30°C at measurable velocity and above 400°C the molecules striking the platinum surface are all decompd. The probability of activation by one collision between nitrogen-pentoxide molecule and platinum surface is about 560 times larger than the probability of activation in the homogeneous reaction at higher press. already studied by other authors. From the reaction velocity the authors obtained the heat of activation, 8—13 Kcal, which are much smaller than the heat of activation of the homogeneous reaction, 20—24.7 Kcal. Stoichiometrically one molecule of nitrogen-pentoxide produces two molecules of a perma-

nent gas, while two molecules produce only one molecule of oxygen in the case of homogeneous reaction. It seems probable that the decompn. take place as follows. $N_2O_5=N_2O+2O_2$. From the above-mentioned points and others, the authors concluded that the reaction is a surface reaction taking place on platinum.

Authors.

Reactions of nitric oxide and oxygen at low pressures and low temperatures. I—II. Y. Hiraki. *J. Chem. Soc. Japan*, **61**, 827—834, 835—838 (1940).—The rate of the reaction between nitric oxide and oxygen at low temps. and low press. was measured by the static and flow method, using a Pirani manometer. At a low press. of 10^{-3} mmHg, and even at a much lower press., the reaction takes place very fast at the temp. of liquid oxygen when the mercury vapour is condensed or condensing on the wall of the reaction vessel. The rate of the reaction is about 10^{29} times larger than the value at these press. and temp. calcd. from the data of homogeneous reaction at higher press. measured by other authors. Therefore, it seems to be a heterogeneous reaction occurring on the wall of the reaction vessel or on the condensed mercury at the temp. of liquid oxygen. Studying this reaction more precisely, it was discovered that the thin film of mercury deposited on the wall of the reaction vessel has strong catalytic action upon this reaction. It was established that the reaction takes place according to the following eq., $2NO+O_2=N_2O_4$ and that the reaction products retard very much the progress of the reaction. It was also established by later studies that the catalytic action of glass surface differs very widely as the species of glass differ.

III. *Ibid.*, **61**, 937—947 (1940).—It was reported that the reaction of nitric oxide and oxygen at low press. and low temps. is a surface reaction and that the mercury which is condensed or is condensing exerts a strong catalytic action upon this reaction. Mercury deposited in advance has a strong catalytic activity, while that condensing during the progress of the reaction or condensed on the reaction products has scarcely any activity. As the amount of mercury increases the catalytic activity also becomes stronger, but it reaches const. value when the amt. of mercury deposited corresponds to about 100 atomic layers, assuming that the deposition takes place uniformly on the glass surface. The adsorptive power of nitric oxide and oxygen on the thin film of mercury was measured and it was obsd. that nitric oxide is adsorbed more or less while oxygen is only sparingly adsorbed. The following eq. of reaction velocity is in good conformity with the rate of the reaction $\frac{-d[O_2]}{dt}=k\frac{[NO][O_2]}{[N_2O_4]}$. It is concluded that the reaction is caused by striking of oxygen molecules on adsorbed nitric oxide molecules adsorbed in advance on the thin film of mercury.

IV. *Ibid.*, **61**, 1005—1013 (1940).—The author discovered a strong catalytic action of a thin film of mercury in the reaction between nitric oxide and oxygen at low temps. and low press. This catalytic action varies markedly with the variation of the temp. of the wall of the reaction vessel, on which the thin film is formed. Below about −140°C. the activity is almost const., but above this temp. it becomes slow and at about −120°C it decreases markedly and suddenly. This phenomenon results from the difference of states of aggregation of mercury atoms. Thin film of mercury deposited at the temp. of liquid air (−183°C) loses markedly its catalytic activity on maintaining the temp. of the reaction vessel at any higher temp. for a few minutes. It probably results from the rearrangement of mercury atoms deposited at random to regular crystalline arrangement by surface migration. The velocity of surface migration of mercury atoms was measured at several temps. by the rate of the decrease of catalytic activity. The energy of activation was found to be 4.3 Kcal. which is required for surface migration. From this value and the heat of vaporisation of mercury and heat of vaporisation from solid body, it is concluded that this migration probably takes place on the nucleus of deposition of mercury in rearrangement of aggregation. Author.